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Derivation of a Cocoa Butter Equivalent from Jojoba Transesterified Ester via a Differential Scanning Calorimetry Index*†

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Abstract: A series of wax ester blends was constructed by transesterifying native jojoba oil with 50–500 g kg^{-1} completely hydrogenated jojoba wax esters. This series, when subjected to a standardised differential scanning calorimetry (DSC) tempering method gave either 1, 2 or 3 enthalpic events which represented the diunsaturated, monounsaturated and saturated species. These species were verified by measuring the melting points of a native and completely hydrogenated jojoba wax ester and also by demonstration that DSC thermograms of a synthetic monounsaturated wax ester possessed an endotherm with a melt between the diunsaturated and completely saturated species. The heats of fusion and heats of crystallisation enthalpies of all three enthalpic events exhibited excellent correlation with the level of saturation. Chemometric indices were devised from heats of fusion and crystallisation enthalpies to estimate the level of saturation in these blends. From these indices and also from regression analyses of each species' individual events we could optimise the level of saturation needed to best mimic the melt and crystallisation properties of cocoa butter. The wax ester blend with 400 g kg^{-1} saturation most closely resembled the thermal properties of cocoa butter where the monounsaturated species of the jojoba blend gave identical thermograms to tempered cocoa butter.

Key words: cocoa butter equivalent, differential scanning calorimetry, jojoba wax, native jojoba, saturated jojoba, transesterified wax ester, index of saturation, chemometric indices, melt temperature, crystallisation temperature.

INTRODUCTION

Differential scanning calorimetry (DSC) thermograms of fatty esters can give valuable information on the melting and crystallising temperatures as well as heats of fusion and crystallisation. This method has been used to investigate cocoa butter equivalents generated from milk fat blends (Md Ali and Dimick 1994), interesterified vegetable oils (Chang *et al* 1990) and interesterified palm oil fractions (Bloomer *et al* 1990). Recently, Sessa *et al* (1996) applied statistical and mathematical techniques to DSC melting curve data to devise an index to determine the level of saturation of transesterified jojoba wax ester blends based on heats of fusion enthalpies. The transesterification involved construction of blends of native jojoba wax ester with 50–500 g kg^{-1} completely hydrogenated jojoba wax esters. The overall objective of our current research was to devise a crystallisation index to estimate the level of saturation of similar blends and then to use both the fusion (Sessa *et al* 1996) and crystallisation indices to select a jojoba saturation blend that most closely mimics the thermal properties of cocoa butter.

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MATERIALS AND METHODS

Natural cocoa butter and the calibration sets consisting of native jojoba wax esters that were transesterified with proportionate blends of completely hydrogenated wax esters to give a series of 50, 100, 150, 200, 300, 400 and 500 g kg^{-1} saturated ester were provided by International Flora Technologies Ltd (Gilbert, AZ, USA).

DSC analysis

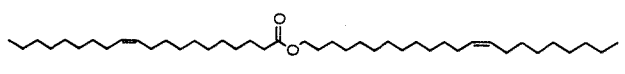
Indices were constructed from data analyses obtained with a Perkin–Elmer DSC 7 equipped with a glove box, Intercooler II and TAS 7 software package (The Perkin–Elmer Corporation, Norwalk, CT, USA). Four replicates of each calibration set were subjected to a standardised DSC tempering method Cj 1-94 with heat/cool cycles (AOCS 1994). (Refer to Sessa *et al* (1996) for experimental details.) Conversion of natural cocoa butter to its most stable crystalline form was achieved by holding cocoa butter at 27°C for an extended time period (Chapman *et al* 1971). Comparison of the stabilised form of cocoa butter with the transesterified jojoba wax ester blend optimised for equivalent thermal properties was performed on a Rheometrics DSC Gold + (Rheometrics Inc, Piscataway, NJ, USA). Samples of about 2 mg were each weighed in gold-plated copper pans to 1 μg accuracy on a Cahn 29 Automatic Electrobalance (Cahn Instruments Inc, Cerritos, CA, USA). After sealing the pans the samples were each scanned from −18°C to 80°C at 10·0°C min^{-1}, sampling every 0·50 s under nitrogen flow at 10 ml min^{-1}.

Statistical analysis

Relationships between heats of crystallisation enthalpies and the level of wax ester saturation were measured by linear regressions in the General Linear Models procedure of the Statistical Analysis Systems software package (SAS 1987). Regression results were examined and compared by *P*-values, R^2 and visual evaluation of residuals. A calibration model was constructed from these data using multilinear regression algorithms to fit the original data.

RESULTS AND DISCUSSION

Jojoba natural wax ester, our starting material, with predominant structural formula:



consists mainly of monoenoic fatty acid esterified with monoenoic alcohol to form a diunsaturated ester.

Sessa *et al* (1996) devised a DSC index based on heat of fusion enthalpy to assess the level of saturation of transesterified jojoba wax esters. These researchers found three enthalpic events in their heat cycle for transesterified blends at 150–500 g kg^{-1} saturation. They labelled these events A, B and C where they attributed event A to the diunsaturated species, B to the monounsaturated species and C to the saturated species. Event A corresponded to the melting point of a jojoba natural wax ester while event C corresponded to the completely saturated species. More recently the author found that the intermediate melting species, designated B, has a melting temperature, based on DSC, that is 10·70°C lower than monounsaturated behenyl eicosenoate synthesised from esterification of behenyl alcohol with eicosenoic acid (unpublished data). Since the synthetic monounsaturated ester melted between the diunsaturated and completely saturated species it was assumed that B represents the monounsaturated species.

As shown in Fig 1, the DSC downscan for crystallisation likewise gave three enthalpic events when the level of saturation exceeded 100 g kg^{-1}. The crystallisation exotherm at the lowest temperature corresponded to the lowest melting endothermic event observed by Sessa *et al* (1996). Hence, this event was labelled A which designates the diunsaturated species. The highest crystallisation exotherm corresponded to the heat of fusion endotherm labelled C and in this paper represents the completely saturated species.

The fusion and crystallisation enthalpies are given in Table 1. In general, the endothermic and exothermic events labelled A, representing the melt and crystallisation enthalpies, decreased in area when the saturation level increased from 100 to 500 g kg^{-1} while events labelled B, representing the monounsaturated species, increased in amplitude over the entire saturation level from 50 to 400 g kg^{-1}. Above 400 g kg^{-1} a drop in its enthalpy was observed. With the saturated

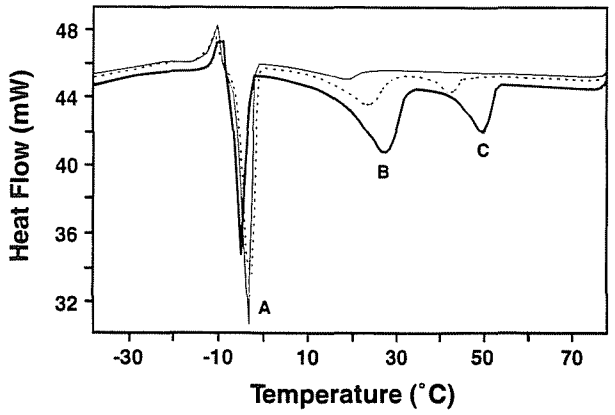


Fig 1. DSC downscans of transesterified jojoba wax esters. Designations for level of saturation: ——, 100 g kg^{-1}; – – –, 200 g kg^{-1}; ——, 300 g kg^{-1}; where A, B and C represent the diunsaturated, monounsaturated and saturated species, respectively (see text).

TABLE 1
DSC fusion and crystallisation enthalpies[a] from transesterified Jojoba wax esters

Saturation level ($g\ kg^{-1}$)	ΔH_f ($J\ g^{-1}$)			ΔH_c ($J\ g^{-1}$)		
	A	*B*	*C*	*A*	*B*	*C*
50	69·88	1·79	—	−71·71	−1·81	—
100	73·94	11·66	1·20	−79·51	−7·62	—
150	71·67	24·73	5·08	−65·04	−17·04	−4·43
200	67·23	38·75	12·60	−58·72	−28·94	−11·62
300	49·95	58·43	16·99	−41·90	−48·80	−16·02
400	41·99	67·38	25·48	−33·64	−54·88	−21·53
500	21·45	61·50	37·51	−15·63	−51·43	−38·13

[a] Designations: ΔH_f, heat of fusion; ΔH_c, heat of crystallisation.

species, labelled C, an increase was noted in amplitude for enthalpies over the entire range from 100 to 500 g kg^{-1} for fusion and from 150 to 500 g kg^{-1} for crystallisation. Linear regressions were derived for each of the three events to include either heat of fusion or heat of crystallisation enthalpies. From the fusion enthalpies $\Delta H_A = 88{\cdot}36 - 1{\cdot}278$ (g kg^{-1} saturation), $R^2 = 0{\cdot}85$ and $\Delta H_C = -7{\cdot}28 + 0{\cdot}864$ (g kg^{-1} saturation), $R^2 = 0{\cdot}95$ followed a straight line function whereas $\Delta H_B = -20{\cdot}23 + 3{\cdot}873$ (g kg^{-1} saturation) $- 0{\cdot}0439$ (g kg^{-1} saturation)^2, $R^2 = 0{\cdot}98$ followed a quadratic function (Sessa *et al* 1996). From the crystallisation enthalpies the best fit was derived from straight-line functions where $\Delta H_A = -79{\cdot}49 + 1{\cdot}238$ (g kg^{-1} saturation), $R^2 = 0{\cdot}82$; $\Delta H_B = 0{\cdot}45 - 1{\cdot}257$ (g kg^{-1} saturation), $R^2 = 0{\cdot}88$; $\Delta H_C = 8{\cdot}82 - 0{\cdot}877$ (g kg^{-1} saturation), $R^2 = 0{\cdot}89$.

In Fig 2 an algorithm was then derived by a multiple regression program applied to the enthalpic events from the crystallisation mode. When the saturated species C is >0, ie above 100 g kg^{-1} saturation level, level of saturation $= 5{\cdot}46 - 0{\cdot}309$ $(\Delta H_B) - 0{\cdot}713$ (ΔH_C), $R^2 = 0{\cdot}94$ whereas when species C = 0, ie below 100 g kg^{-1} saturation level, level of saturation $= 24{\cdot}46 + 0{\cdot}279$ $(\Delta H_A) - 0{\cdot}453$ (ΔH_B), $R^2 = 0{\cdot}91$. The standard errors for predictions were approximately the same over the range from 50 g kg^{-1} to 500 g kg^{-1} saturation level. From these crystallisation data and also from the previously reported fusion data (Sessa *et al* 1996) the derived algorithms can serve as a research tool in process development to evaluate with a high degree of precision the level of saturation in transesterified jojoba wax ester blends.

The major objective of this research was to use the above derived equations to optimise a level of saturation in the transesterified jojoba wax ester blends that most closely mimics the melting and crystallising properties of cocoa butter. Cocoa butter is a triglyceride consisting predominantly of oleic, palmitic and stearic acids. It can exist in six polymorph crystal forms (Duurland and Smith 1995). The cocoa butter used in our research gave a DSC thermogram with fusion and crystallisation enthalpic illustrated in Fig 3. The heat of fusion endotherm possessed a peak temperature of

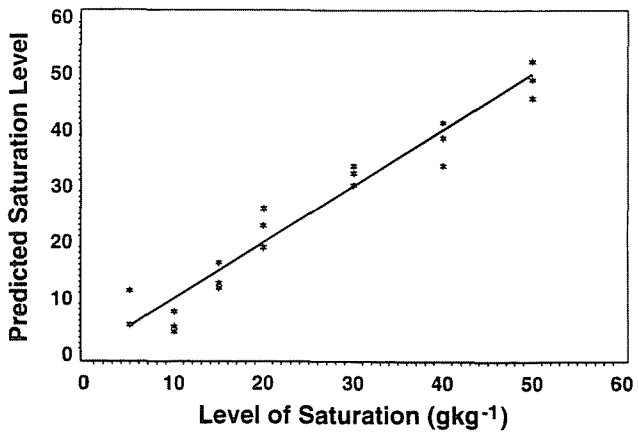


Fig 2. Actual data vs predictions based on crystallisation enthalpies (ΔH) where the level of saturation $= 5{\cdot}46 - 0{\cdot}309$ $(\Delta H_B) - 0{\cdot}713$ (ΔH_C), $R^2 = 0{\cdot}94$ when saturated species C > O, and level of saturation $= 24{\cdot}46 + 0{\cdot}279$ $(\Delta H_A) - 0{\cdot}453$ (ΔH_B), $R^2 = 0{\cdot}91$ when saturated species C = 0. ΔH_A, ΔH_B, ΔH_C enthalpies of diunsaturated, monounsaturated and saturated species, respectively (see text).

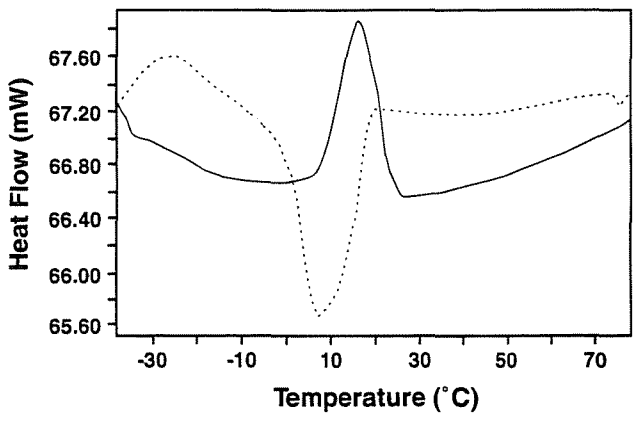


Fig 3. DSC thermograms of natural cocoa butter. ——, Upscan; – – –, downscan.

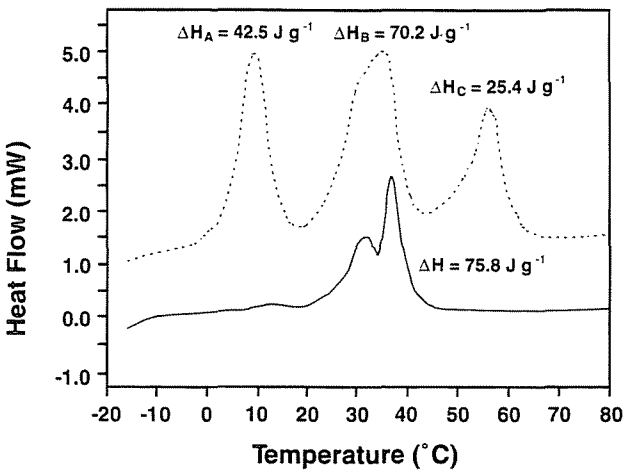


Fig 4. DSC thermograms of 400 g kg^{-1} saturated jojoba wax ester (——) and cocoa butter as β forms when tempered several months at 27°C (– – –).

16·42°C with enthalpy of 71·97 J g^{-1} while the crystallisation exotherm peaked at 7·73°C and possessed an enthalpy of −74·53 J g^{-1}. Its melting point, determined by AOCS recommended procedure Cc 18-80 (AOCS 1994), using a Mettler FP90 Central Processor equipped with a FP83HT dropping point cell, was 25·8°C which corresponded to a mixture of α and β'_2 crystalline forms according to Duurland and Smith (1995). According to these authors, this crystalline polymorphic form is unstable. Upon several months of tempering at 27°C this cocoa butter polymorph reverted mainly to a β_1 crystal form with a peak endothermic event at 36·72°C shown in the thermogram of cocoa butter in Fig 4. When cocoa butter was tempered at 27°C for several months it possessed trace amounts of α polymorph and fusion endotherms indicative of β_2 and β_1 polymorphic forms with a total enthalpy of 75·8 J g^{-1}. These β crystalline forms equated to the melt temperature of the monounsaturated species of transesterified jojoba wax ester where maximum enthalpy of the monounsaturated species of wax ester was obtained at 400 g kg^{-1} saturation level. In Fig 4 the monounsaturated species of transesterified jojoba wax ester blend at 400 g kg^{-1} saturation level possessed an identical endothermic event with an enthalpy of 70·2 J g^{-1}. Still more research is needed to determine whether the monoene species can be successfully and economically fractionated. Compatibility studies of cocoa butter and wax ester are definitely essential to determine the impact of the blend on melt temperature as well as texture of the final product.

CONCLUSIONS

We devised mathematical indices based on heats of crystallisation enthalpies as well as heats of fusion enthalpies to define the level of saturation in transesterified wax ester blends and used them to select the optimum level of saturation needed for obtaining a cocoa butter equivalent. We demonstrated that the monounsaturated species of the jojoba transesterified wax ester blends possesses similar thermal characteristics to cocoa butter in its most stable β polymorphic forms.

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